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Thermally Stimulated Conductivity Studies of Trapping Centers in Alkali Borosilicate Glasses*

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Thermally stimulated conductivity studies have been performed on unirradiated borosilicate glasses made to contain various amounts of sodium, lithium, nickel, and iron oxides. Measurements were made between 77°K and 570°K. All the samples gave one or more conductivity peaks below room temperature. Analysis of the initial rise slope of the conductivity peaks of the various samples gave trapping level energies ranging from 0.1 to 1.9eV. The shape and temperature of the maximum of most of the peaks changed on each measurement cycle. A few samples exhibited a common peak, that formed on annealing.

Introduction

The electrical conductivity of alkali-borosilicate glasses is related to the defect structure of the glass. The conductivity in this glass system is basically ionic. However, as indicated by the studies of Murray (1-2), there is some electron conduction present, that is closely connected to the ionic conduction. Under application of an electric field to the glass, a steady state current is produced by the flow of electrons between the metal electrodes and the glass surface. The electrons reduce the space charge from the alkali ion build up. The alkali ions in a borosilicate glass are responsible for some of the non-bridging oxygen ions in the glass structure. These non-bridging oxygen ions constitute part of the defect structure of the glass. The alkali ions form ionic bonds to some of these non-bridging oxygen ions. As the alkali ions migrate through the glass, mobile defect states are produced.

The structure of alkali-borosilicate glasses of low alkali concentration can be pictured (3-5) as an alkali borate glass diluted by SiO_2. Thus there is a mixture of BO_3 units and BO_4 units with the fraction of BO_4 units equal to R, the ratio of alkali oxide to boron oxide. Studies indicate that in this composition region no non-bridging oxygens are formed. For increasing concentrations of alkali ions above R = 0.5, the number of four coordinated borons will reach a maximum and then decrease. Increasing amounts of non-bridging oxygen atoms are formed with increasing concentrations of alkali ions in this region of R greater than 0.5.

Brungs and McCartney (4) propose that at a sodium to boron ratio of one, the rigidity of the borosilicate glass network passes through a maximum due to a corresponding maximum in the formation of four coordinated borons. They suggest that when the sodium to boron ratio is greater than one, non-bridging oxygen atoms in the $(SiO_4)^-$ sites form, causing the decrease in network rigidity.

The conductivity of borate, silicate, and borosilicate glasses that contain alkali ions has been studied extensively (6-7) and has been found to be mostly ionic. The ionic conductivity is a thermally activated process. The activation energy is commonly observed to be in the range 0.6 to 1.2 eV and to decrease with increasing alkali concentration. The activation energy is often observed to have different values for different temperature regions. Studies of lithium ion transport in both silicate and borate glasses (8) show a region around room temperature with an activation energy in the range 0.5 to 0.7 eV that was related to a long-range motional process and a region at lower temperatures (100-300^{o}K) with an activation energy in the range .08 to .26 eV that was related to a short-range motional process. A study on the affect of crystallinity on the ionic conductivity in a $LiAlSiO_4$ glass-ceramic system (9), found that the activation energy is independent of the percent crystallinity up to about 55%, after which it increases. When the alkali content of a glass system is increased by the introduction of a second alkali ion into the system, many of the physical properties of the glass are observed to vary in a very non-linear manner. This

has been called the "mixed alkali" effect. A review of the subject is given by Isard (10). The effect is observed for alkali ion concentrations greater than 10%. The conductivity of a mixed alkali glass system is observed to have a minimum and its activation energy a maximum, when the two alkali oxides are present in about equal proportion. A theory for the effect is given by Hendrickson and Bray (11).

Although there is some electronic transport present in these oxide glasses, few studies have been made on its effect on the glass conductivity. A good review of the electrical properties of glasses, including current views on the electronic band structure in glasses is given by Owen (12). There is increasing evidence that an important electronic transport mechanism for amorphous semiconductors and for oxide glasses is hopping through localized states (12-13). These localized states consist of band tail states and gap states. The tail states are due to the disorder of the glass network, while the gap states are from structural defects, such as non-bridging oxygen atoms or dangling bonds.

Several defect centers have been proposed to occur in SiO_2 structures (14-19). These centers have often been studied and characterized by electron spin resonance and thermoluminescence studies of irradiated silicate glass and quartz. Schreurs (16), for example, has proposed models for trapped hole centers in irradiated alkali silicate glasses. He has proposed the existance of a hole center, HC_1, which is a hole trapped on a Si-O network having two non-bridging oxygens, and a hole center, HC_2, which is a hole trapped on a Si-O network having three non-bridging oxygens. Another kind of defect center that has been found in

irradiated quartz is the $E_{\gamma c}^{1}$ center (17) which is proposed to be an electron trapped on a silicon bonded to just three oxygens. Strained silicon-oxygen bonds with abnormal bonding angles, also, produce trapping centers (18).

In this paper the method of thermally stimulated current (TSC) is used to study the trapping centers in several different non-irradiated alkali borosilicate glass systems. In this method the sample is heated at a constant rate from some low temperature. The current that results as the carriers are thermally released from trapping centers exhibits peaks. This method is often used to study trapping states in high resistance semiconductors and insulators. Good reviews of the method are given by Bube (20), and by Milnes (21).

The energy of the trapping levels can in principle be determined from analysis of the thermally stimulated current curves. The conductivity is given by $\sigma = e \mu n$, where e is the electronic charge, μ the mobility of the carriers and n is the density of electrons in the conduction band. The density n is given by (21).

$$\frac{dn}{dt} = -\frac{n}{\tau} - \sum_i \left\{ - n_i N_c \sigma_i v \exp\left(-\frac{E_i}{kT} \right) + n \left(N_i - n_i\right) \sigma_i v \right\}$$

where n_i is the density of electrons in the i th impurity level, N_c the effective density of states in the conduction band, σ_i the capture cross section of the i th level, v the thermal velocity of the electrons, N_i is the density of the i th level, τ the recombination time

of the electrons, and E_i the energy level of the trap below the conduction band. Analysis of these equations is difficult and generally many assumptions and approximations are made in order to obtain information from the TSC curves. Considering that only one trap level contributes at a time, that the recombination time is long, that steady state conditions exist, and that the quantities N_i, n_i, Nc and σ_i vary slowly with temperature near the conductivity peaks, we obtain

$$n = \frac{N_c\, n_i}{(N_i - n_i)} \exp\left(-\frac{E_i}{kT}\right)$$

Thus the trap level energy can be determined from the initial rise slope of the plot of the logarithm of the conductivity versus the inverse temperature.

Experimental

The samples were prepared using typical glass preparation techniques. The appropriate amounts of reagent grade chemicals were heated in a crucible for about an hour at 1000°C. The sodium, lithium, and nickel were introduced in the form of carbonates. The iron was introduced as ferric oxide. The glass melt was rapidly quenched by squashing it between two metal plates. This process produced flat samples about 1 mm thick. A variety of compositions were studied. The batch compositions of the samples are given in Table I. All of the samples, except one, had an alkali oxide to boron oxide ratio greater than one. All the samples had the same silicon oxide to boron oxide ratio.

Two terminal dc electrical conductivity measurements were performed on the glass samples between 77°K and about 570°K. Electrodes were painted on the samples with silver paint. In performing the measurements a voltage of 20 volts was applied to the sample.

The sample was cooled at 77°K, then measurements were taken as the sample was heated at a constant rate of about 0.16°K/sec.

Results

Some representative thermally stimulated conductivity curves are given in Figs. 1-4. All of the samples exhibit at least one peak below room temperature. One sample (914) gave a high temperature peak. Some of the samples gave two or three well resolved conductivity peaks. In Table II the values for the temperature of the peak maximum, T_m, and the trapping level energy E_i are given for the curves shown. The energy values were determined from a least squares fit of the data from the initial rise slope of the curves. A wide range of values (0.17 to 1.0 eV.) for the trapping level energy were obtained from the conductivity peaks. One similarity among the conductivity peaks was observed in the curves of samples 906, 907, 910, and 911. All these samples exhibited a peak in the narrow temperature range 292° to 299°K with energy value 0.17 to 0.19 eV. This common peak often was bearly observable on the first measurement run, but would form on subsequent runs.

The conductivity peaks, in general, change shape and position on each subsequent run of the 77°K to 570°K measurement cycle. The peaks

may shift slightly to a higher or lower temperature, and they may increase or decrease in magnitude. The initial rise slopes also change. Sometimes a new peak will appear or one will disappear. For example, on a second run of sample 914, the high temperature peak, observed in Figure 4, was shifted to a lower temperature just above room temperature. The low temperature peak for this sample was also shifted slightly to a lower temperature. The peaks for samples 902 and 905, on the second run, shifted to a lower temperature and increased slightly in magnitude. The peaks for samples 906 and 907 would increase on one run and decrease on another. Some of the peaks had large changes in magnitude. Also the various peaks of each of the samples 906 and 907 gave temperature shifts in opposite directions.

There was some apparent influence of sample composition on the conductivity of a few of the samples. Samples 914 was the only sample that exhibited a high temperature peak. This also was the only sample without lithium ions. The sample 907, which contains a high concentration of iron ions, gave curves with more distinct structure than the other samples. Also some of the conductivity peaks for this sample exhibited on successive measurement cycles greater changes in magnitude than observed in the other samples.

At high temperatures the conductivity of the glasses should be essentially due to ionic conductivity. Ionic conductivity is thermally activated and should change exponentially with reciprocal temperature. The ionic conductivity activation energies E_a, determined from the high temperature part of conductivity curves, are included in Table II.

Summary and Discussion

The ionic conductivity activation energies E_a for all the samples, except 914, are close in value. This is reasonable since all the samples, except 914, have about the same sodium and lithium concentrations. The difference between the values for sample 914 and those of the other samples is a manifestation of the mixed alkali effect.

All the glass samples gave one or more conductivity peaks in the region from 200° to 300°K. The sample 914 was the only sample that gave a peak well above room temperature. The composition of sample 914 differs greatly from the other glass samples. It contains only sodium ions, and its ratio of alkali oxide to boron oxide is less than one. The structural studies (3-5) of the sodium borosilicate glass system indicate that for a Na_2O to B_2O_3 ratio between 0.5 and 1 that there should be non-bridging oxygens present, but probably not in the silicon-oxygen sites. Thermoluminescence studies (19) of a sodium silicate glass system that was irradiated gave some high temperature glow curves. So there are defect structures that can form in the silicon-oxygen network to give the high temperature conductivity peaks. Further studies will have to be made to determine the relationship of the high temperature peak to the glass composition and a possible defect center. The analysis of the low temperature curves gave a range of trapping level energies from 0.1 to 1.9 eV. However for some of the peaks the analysis is questionable, since the position and shape of the curves changed on each measurement cycle. Also the shape of

some of the curves indicated that there may be overlapping peaks.

The stable peak, observed in the range from 292° to 299°K for several of the samples, suggests that there is a distinct defect center in those glass samples with a level energy of about 0.18 eV.

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Figure Captions

Figure 1 — Plot of conductivity versus inverse temperature for samples 902 and 905.

Figure 2 — Plot of conductivity versus inverse temperature for samples 906 and 907. The numbers indicate part of curves used in calculation of values in Table II.

Figure 3 — Plot of conductivity versus inverse temperature for samples 910 and 911. The numbers indicate the part curve used in calculation of values in Table II.

Figure 4 — Plot of conductivity versus inverse temperature for samples 913 and 914. The numbers indicate the part of the curve used in the calculation of values in Table II.

TABLE I. Sample batch compositions (molar %), ratio of alkali oxide to boron oxide, and ratio of silicon oxide to boron oxide.

SAMPLE	Na_2O	Li_2O	B_2O_3	SiO_2	NiO	Fe_2O_3	$\frac{Na_2O+Li_2O}{B_2O_3}$	$\frac{SiO_2}{B_2O_3}$
902	16.681	15.952	20.254	32.69	8.272	6.149	1.611	1.614
905	16.183	15.476	19.65	31.71	8.0258	8.95	1.611	1.614
906	18.185	17.39	22.08	35.638	—	6.703	1.611	1.614
907	17.04	16.297	20.693	33.398	—	12.567	1.611	1.614
910	18.59	17.78	22.57	36.438	4.611	—	1.611	1.614
911	15.109	14.449	18.346	29.61	22.48	—	1.611	1.614
913	19.578	18.62	23.64	38.158	—	—	1.616	1.614
914	24.058	—	29.952	46.889	—	—	.828	1.614

TABLE II. Conductivity Results

SAMPLE	$T_m(^oK)$	E_i(eV)[a]		E_a(eV)
902	266.6	.41		.74
905	229.8	1.04		.66
906	229.8	.80	(1)	.79
	298.5	.19	(2)	
907	243.9	.29	(3)	.73
		.66	(4)	
	263.1	1.94	(5)	
	294.1	.19	(6)	
910	259.7	.24	(1)	.86
		1.2	(2)	
	292.4	.17	(3)	
911	243.9	.31	(4)	.86
	296.3	.17	(5)	
913	285.7	.42	(1)	.84
		.26	(2)	
914	285.7	1.3	(3)	.44
		.60	(4)	
	425.5	.63	(5)	

[a] The numbers in parenthesis correspond to the numbers on the conductivity curves, indicating that portion of the curves used to determine the values.